Supporting information

Unveiling the mechanism of CO_2 electroreduction to C_1 and C_2 products on ordered double transition metal MXenes.

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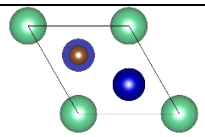
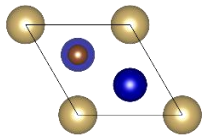
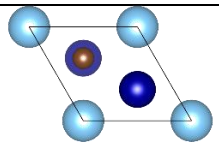
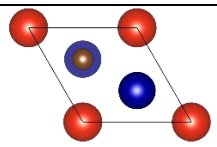
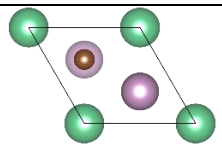
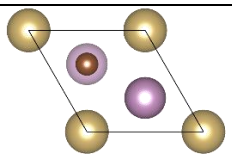
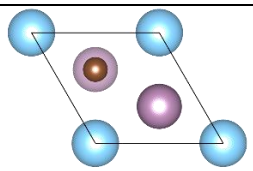
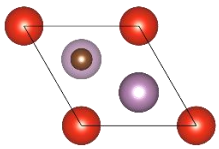
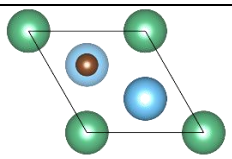
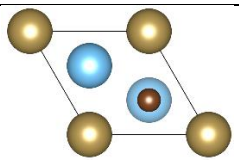
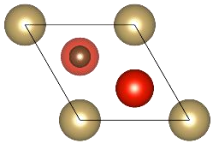
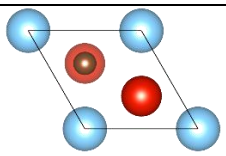
Fig. S9: Variation of energy versus the AIMD simulation time for Mo_2TaC_2 for 6 ps at 600 K. The insets are the top views of snapshots of configurations.

Table S1: *Optimized geometries of Unit cells of M-Xenes along with calculated lattice parameters.*

System	Structure	Lattice parameters
Cr_2NbC_2		a=b=3.175 Å c=5.874 Å α=β=90º γ=120º
Cr_2TaC_2		a=b=3.164 Å c=5.816 Å α=β=90º γ=120º
Cr_2TiC_2		a=b=3.035 Å c=6.242 Å α=β=90º γ=120º
Cr_2VC_2		a=b=3.006 Å c=6.172 Å α=β=90º γ=120º
Mo_2NbC_2		a=b=3.282 Å c=6.584 Å α=β=90º γ=120º
Mo_2TaC_2		a=b=3.134 Å c=7.050 Å α=β=90º γ=120º
Mo_2TiC_2		a=b=3.167 Å c=6.712 Å α=β=90º γ=120º
Mo_2VC_2		a=b=3.188 Å c=6.438 Å α=β=90º γ=120º
Ti_2NbC_2		a=b=3.157 Å c=7.143 Å α=β=90º γ=120º

Ti_2TaC_2		**a=b=3.089 Å c=7.480 Å** **α=β=90º γ=120º**
V_2TaC_2		**a=b=3.091 Å c=6.681 Å** **α=β=90º γ=120º**
V_2TiC_2		**a=b=3.005 Å c=6.816 Å** **α=β=90º γ=120º**

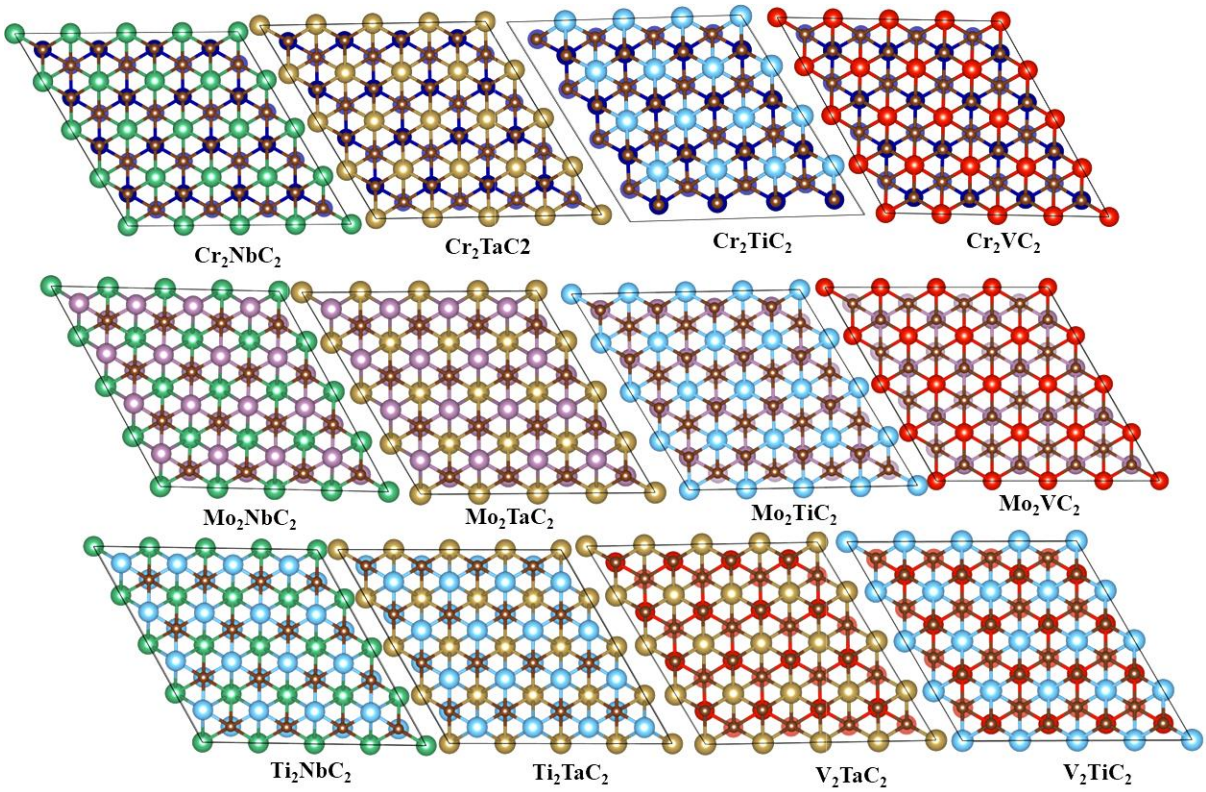


Fig S1: *Top view of optimised structures of $M'_2M''C$ MXenes where M' can be Cr, Mo, Ti, V and M'' be Nb, Ta, Ti, and V.*

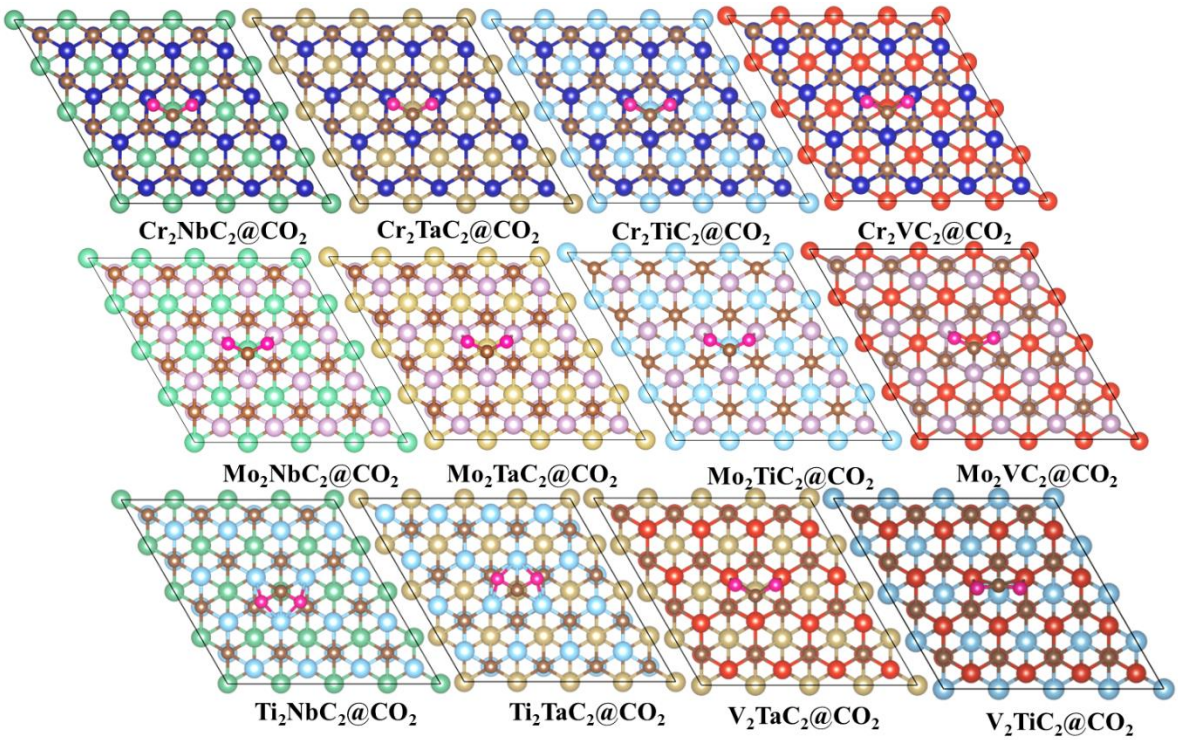


Fig. S2: *Top view of lowest energy configuration of CO_2 adsorbed on MXenes.*

Table S2: *Calculated Bader charge of CO_2 adsorbed on MXenes.*

Catalyst	**C (e)**	**O (e)**	**Net Bader charge (e)**
Cr_2NbC_2	0.86	-1.06	-1.26
Cr_2TaC_2	0.87	-1.06	-1.25
Cr_2TiC_2	0.82	-1.05	-1.28
Cr_2VC_2	0.82	-1.05	-1.28
Mo_2NbC_2	0.87	-1.05	-1.23
Mo_2TaC_2	0.87	-1.05	-1.23
Mo_2TiC_2	0.88	-1.05	-1.22
Mo_2VC_2	0.86	-1.06	-1.26
Ti_2NbC_2	0.67	-1.13	-1.59
Ti_2TaC_2	0.59	-1.12	-1.65
V_2TaC_2	0.71	-1.06	-1.41
V_2TiC_2	1.07	-1.12	-1.17

Table S3: *Calculated activation barrier of C-O dissociation mechanism for three best catalysts.*

Catalyst	ΔG_{CO} (eV)	ΔG_{CO2} (eV)	ΔGa (eV)
Mo_2TaC_2	-1.38	-1.9	0.51
Mo_2TiC_2	-1.66	-2.18	0.52
Mo_2VC_2	-1.82	-2.45	0.63

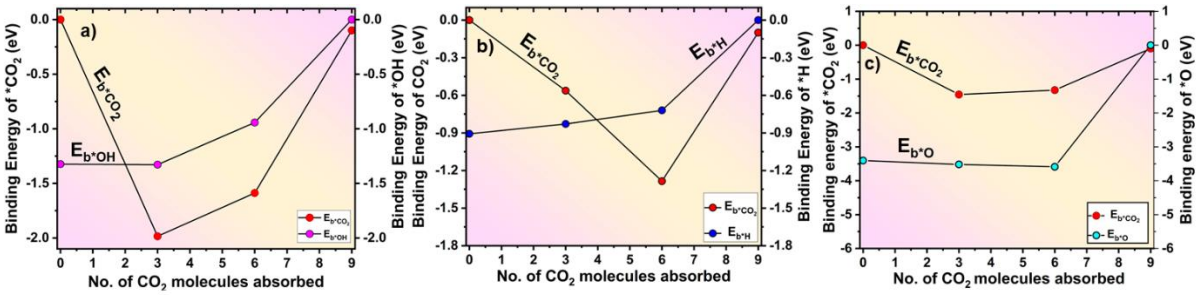


Fig. S3: *Phase plot comparing CO_2 binding energy with a) binding energy of *OH b) binding energy of *H c) binding energy of *O*

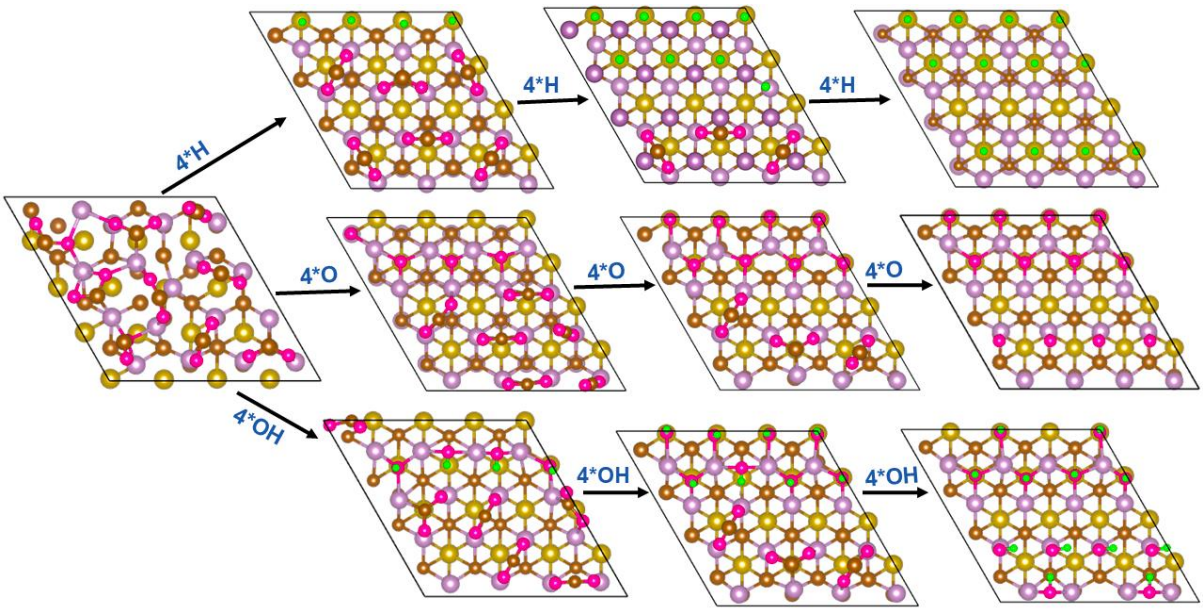
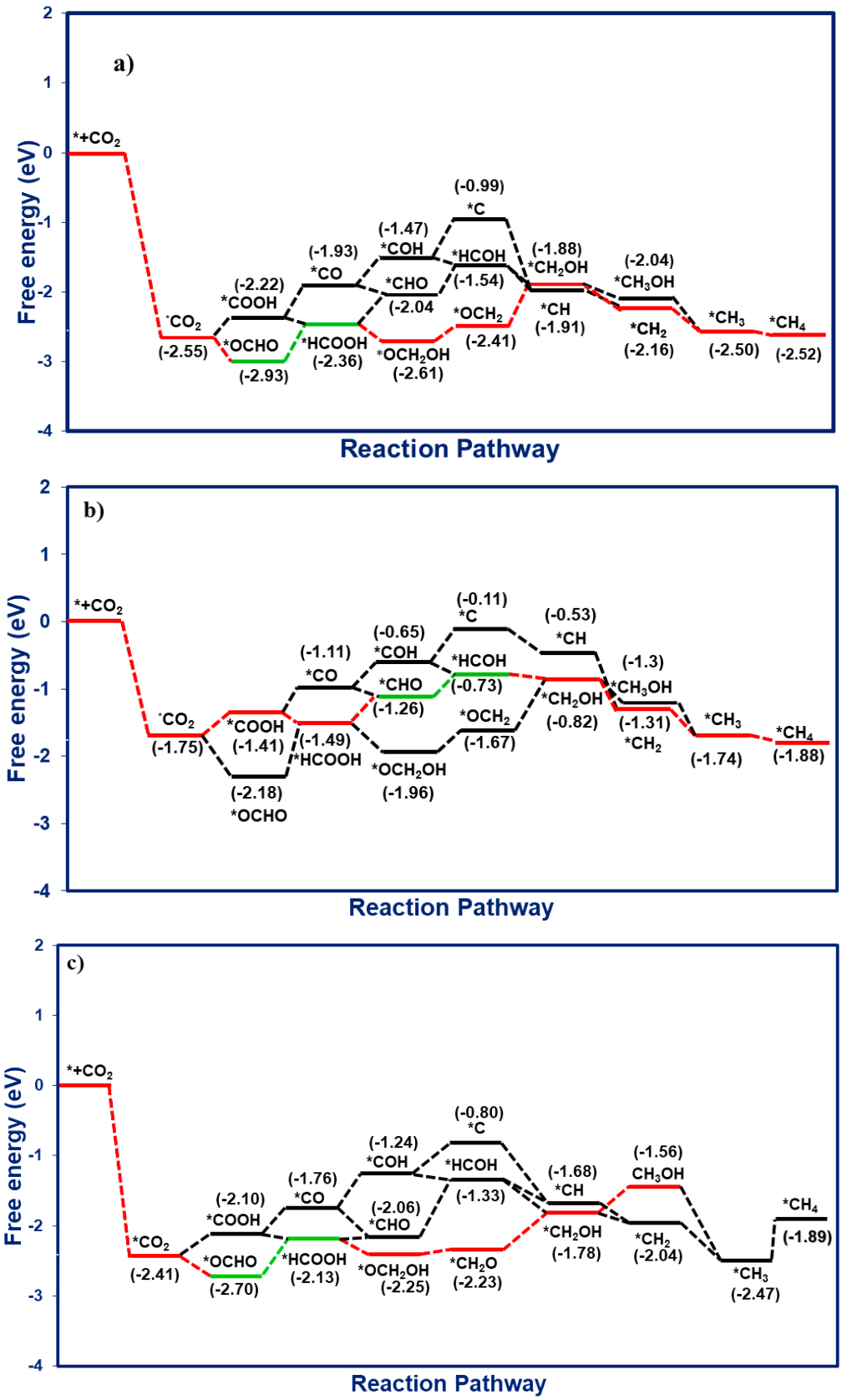
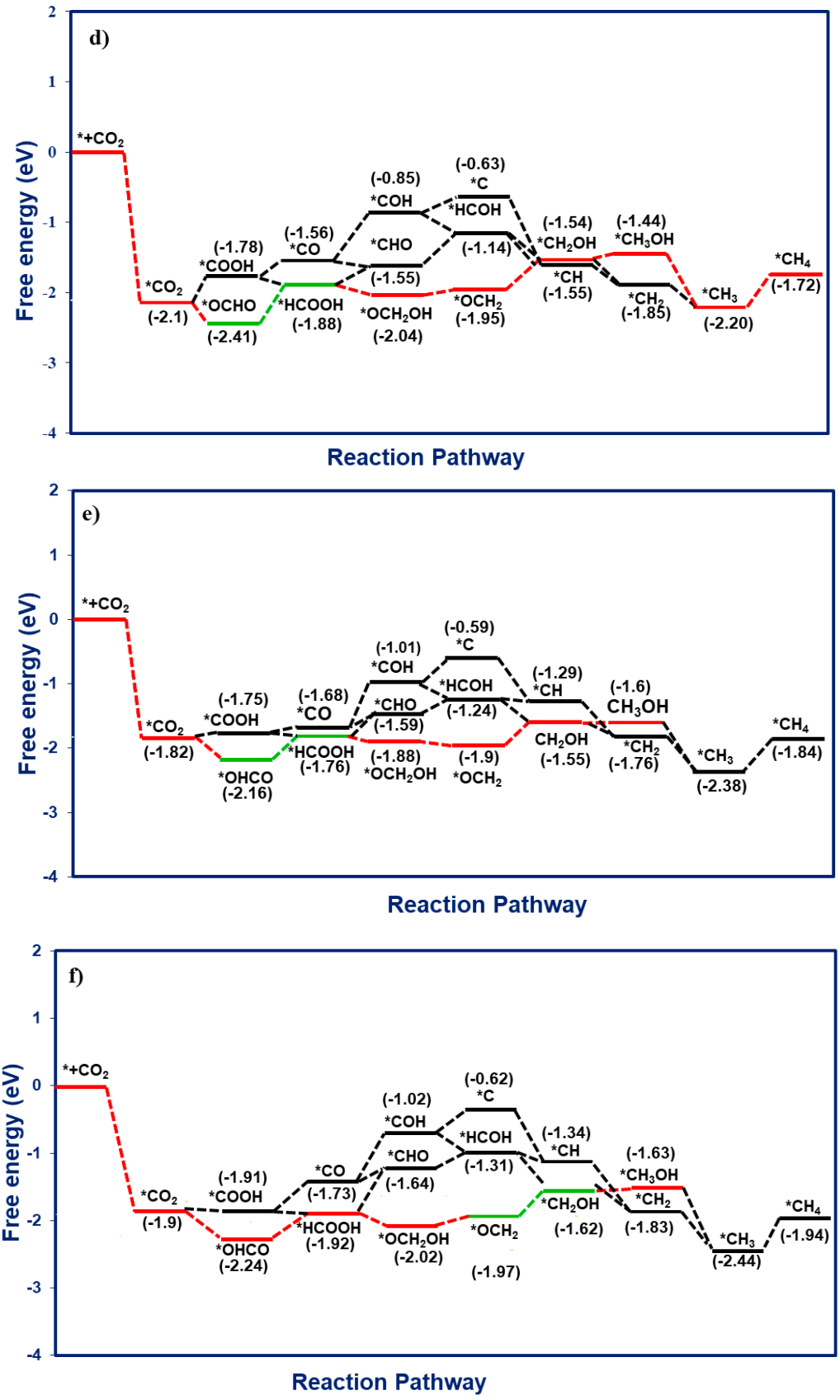
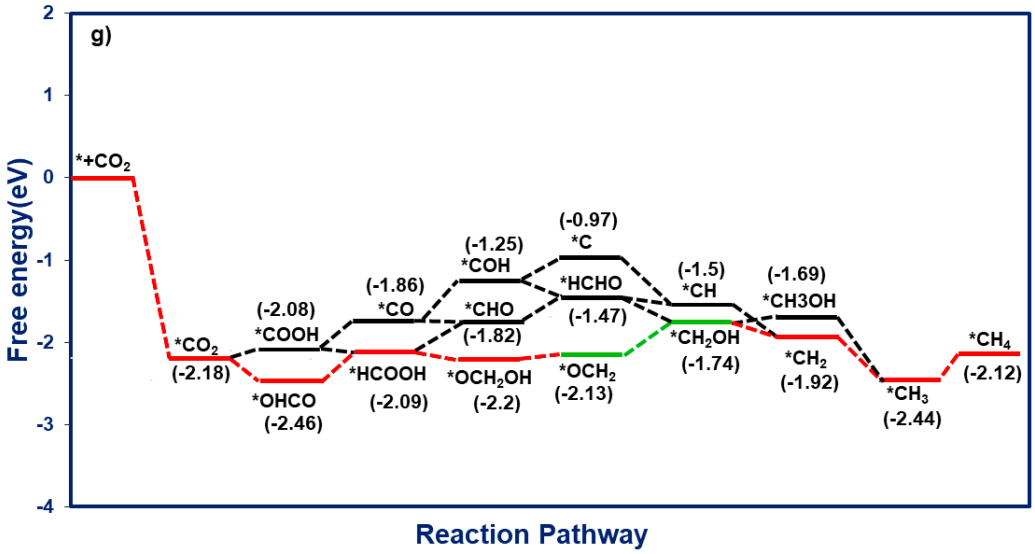
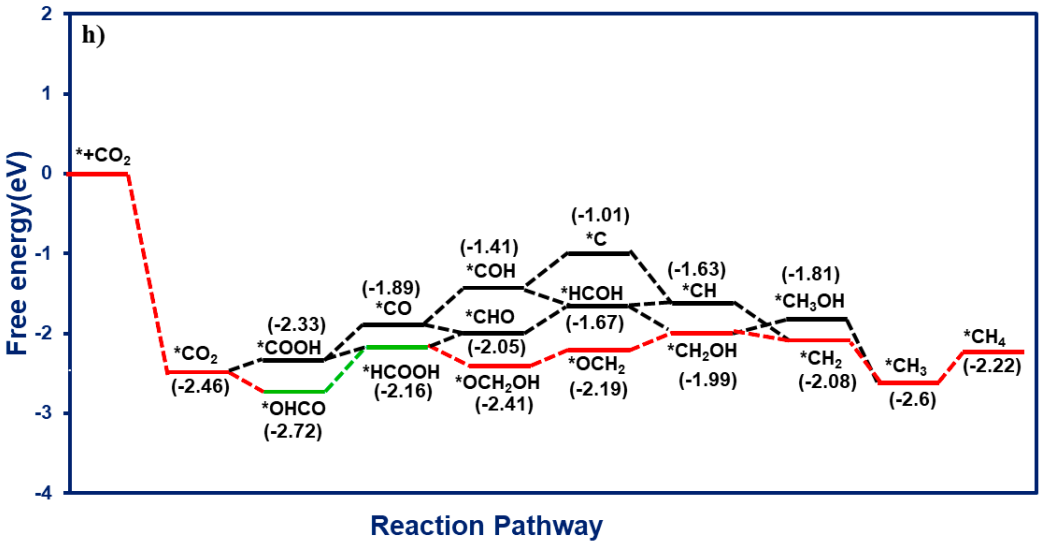


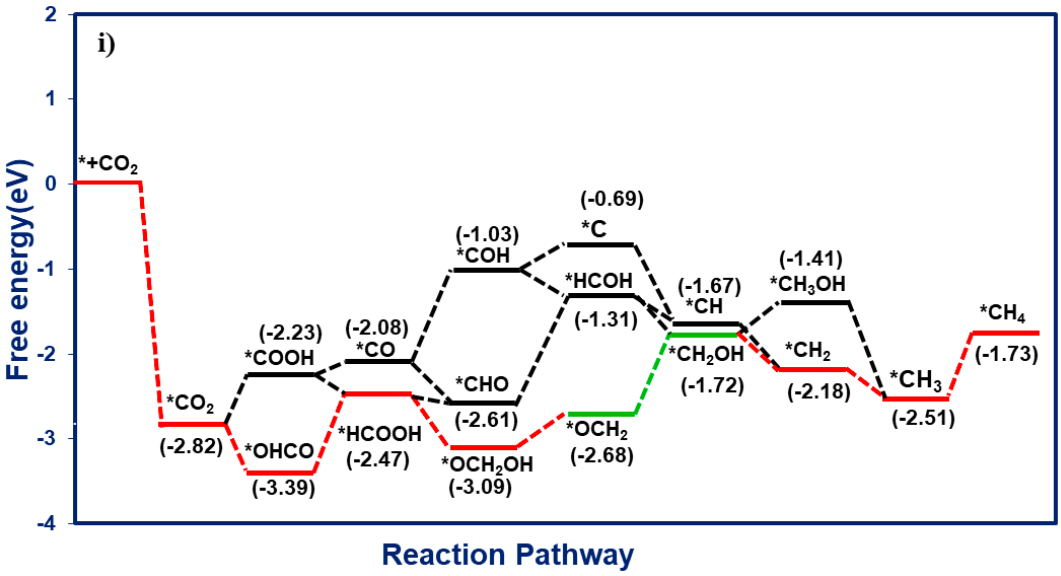
Fig. S4: *Behaviour of CO_2 adsorption on the catalyst surface with other co-adsorbates (*H, *O, *OH).*


a)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2
(-2.55)
(-2.22)
*COOH
*OCHO
(-2.93)
(-1.93)
*CO
*HCOOH
(-2.36)
(-1.47)
*COH
*CHO
(-2.04
*OCH2OH
(-2.61)
(-0.99)
*C
*HCOH
(-1.54)
*OCH2
(-2.41)
(-1.88)
*CH2OH
*CH
(-1.91)
(-2.04)
*CH3OH
*CH2
(-2.16)
*CH3
(-2.50)
*CH4
(-2.52)
b)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2
(-1.75)
*COOH
(-1.41)
(-2.18)
*OCHO
(-1.11)
*CO
(-1.49)
*HCOOH
(-0.65)
*COH
*CHO
(-1.26)
*OCH2OH
(-1.96)
(-0.11)
*C
*HCOH
(-0.73)
*OCH2
(-1.67)
(-0.53)
*CH
*CH2OH
(-0.82)
(-1.3)
*CH3OH
(-1.31)
*CH2
*CH3
(-1.74)
*CH4
(-1.88)
c)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2
(-2.41)
(-2.10)
*COOH
*OCHO
(-2.70)
(-1.76)
*CO
*HCOOH
(-2.13)
(-1.24)
*COH
(-2.06)
*CHO
*OCH2OH
(-2.25)
(-0.80)
*C
*HCOH
(-1.33)
*CH2O
(-2.23)
(-1.68)
*CH
*CH2OH
(-1.78)
(-1.56)
CH3OH
*CH2
(-2.04)
*CH3
(-2.47)
*CH4
(-1.89)


d)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2
(-2.1)
*COOH
(-1.78)
*OCHO
(-2.41)
*CO
(-1.56)
*HCOOH
(-1.88)
*COH
(-0.85)
*CHO
(-1.55)
*OCH2OH
(-2.04)
*C
(-0.63)
*HCOH
(-1.14)
*OCH2
(-1.95)
*CH2OH
(-1.54)
*CH
(-1.55)
*CH3OH
(-1.44)
*CH2
(-1.85)
*CH3
(-2.20)
*CH4
(-1.72)
e)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2
(-1.82)
*COOH
(-1.75)
*OHCO
(-2.16)
*CO
(-1.68)
*HCOOH
(-1.76)
*COH
(-1.01)
*CHO
(-1.59)
(-1.88)
*OCH2OH
*C
(-0.59)
*HCOH
(-1.24)
(-1.9)
*OCH2
*CH
(-1.29)
CH2OH
(-1.55)
CH3OH
(-1.6)
*CH2
(-1.76)
*CH3
(-2.38)
*CH4
(-1.84)
f)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2
(-1.9)
*COOH
(-1.91)
*OHCO
(-2.24)
*CO
(-1.73)
*HCOOH
(-1.92)
*COH
(-1.02)
*CHO
(-1.64)
*OCH2OH
(-2.02)
*C
(-0.62)
*HCOH
(-1.31)
*OCH2
(-1.97)
*CH
(-1.34)
*CH2OH
(-1.62)
*CH3OH
(-1.63)
*CH2
(-1.83)
*CH3
(-2.44)
*CH4
(-1.94)


g)
Free energy(eV)
Reaction Pathway
*+CO2
*CO2
(-2.18)
(-2.08)
*COOH
*OHCO
(-2.46)
(-1.86)
*CO
*HCOOH
(-2.09)
(-1.25)
*COH
*CHO
(-1.82)
*OCH2OH
(-2.2)
(-0.97)
*C
*HCHO
(-1.47)
*OCH2
(-2.13)
(-1.5)
*CH
*CH2OH
(-1.74)
(-1.69)
*CH3OH
*CH2
(-1.92)
*CH3
(-2.44)
*CH4
(-2.12)


h)
Free energy(eV)
Reaction Pathway
*+CO2
*CO2
(-2.46)
(-2.33)
*COOH
*OHCO
(-2.72)
(-1.89)
*CO
*HCOOH
(-2.16)
(-1.41)
*COH
*CHO
(-2.05)
*OCH2OH
(-2.41)
(-1.01)
*C
*HCOH
(-1.67)
*OCH2
(-2.19)
(-1.63)
*CH
*CH2OH
(-1.99)
(-1.81)
*CH3OH
*CH2
(-2.08)
*CH3
(-2.6)
*CH4
(-2.22)


i)
Free energy(eV)
Reaction Pathway
*+CO2
*CO2
(-2.82)
(-2.23)
*COOH
*OHCO
(-3.39)
(-2.08)
*CO
*HCOOH
(-2.47)
(-1.03)
*COH
*CHO
(-2.61)
*OCH2OH
(-3.09)
(-0.69)
*C
*HCOH
(-1.31)
*OCH2
(-2.68)
(-1.67)
*CH
*CH2OH
(-1.72)
(-1.41)
*CH3OH
*CH2
(-2.18)
*CH3
(-2.51)
*CH4
(-1.73)

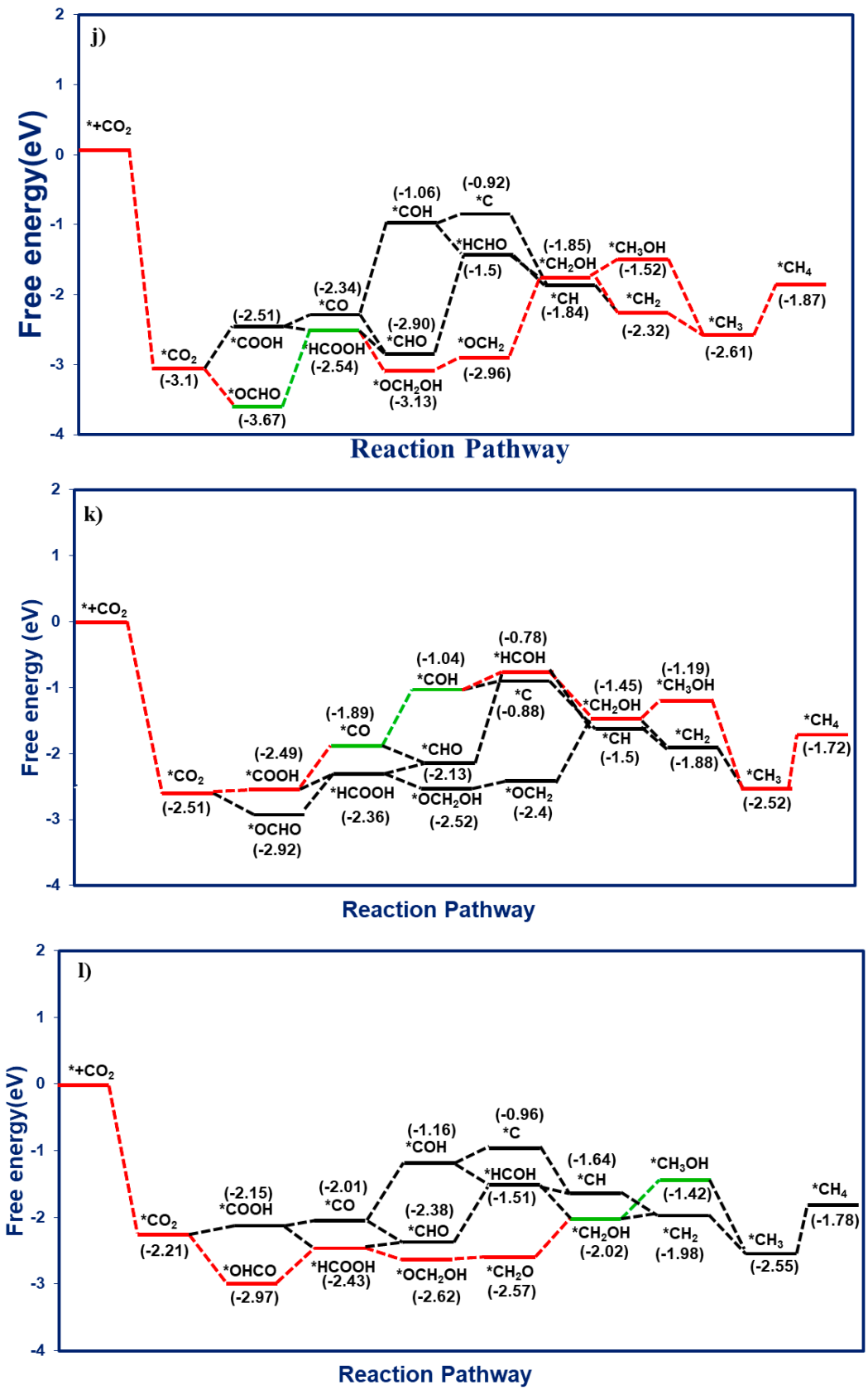
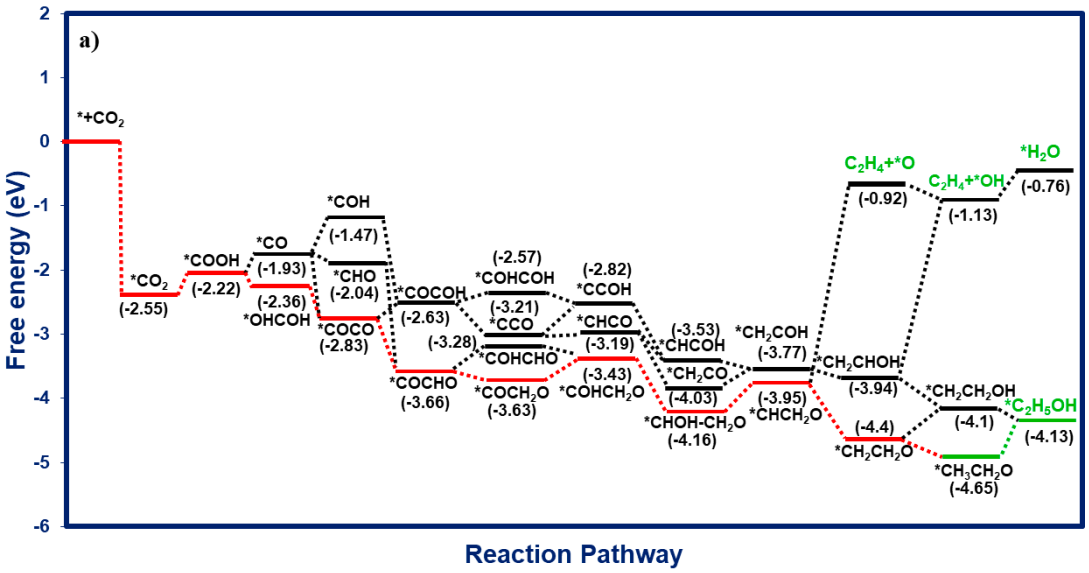
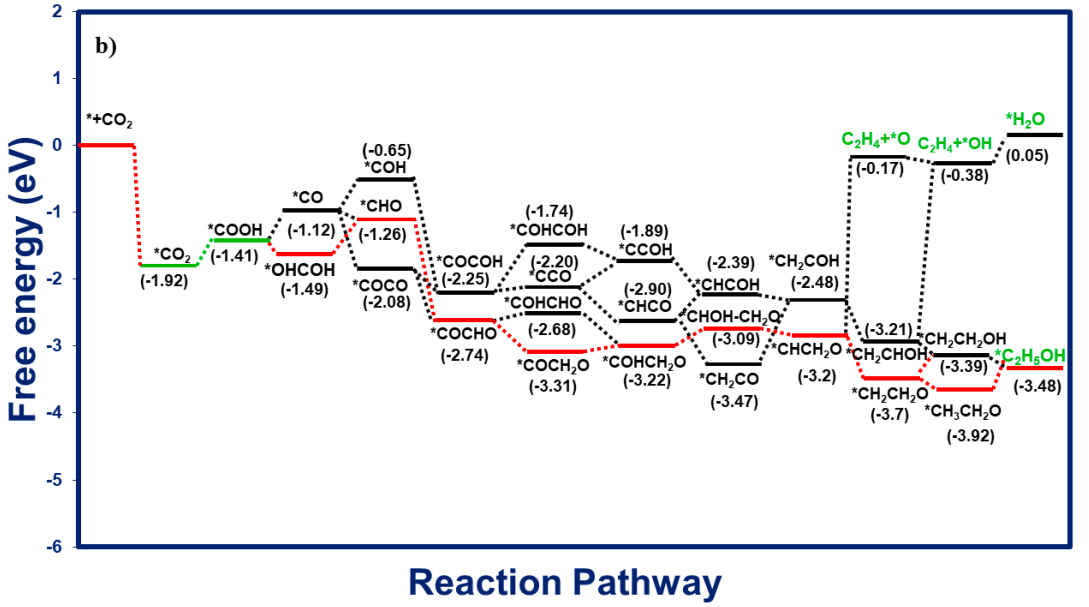
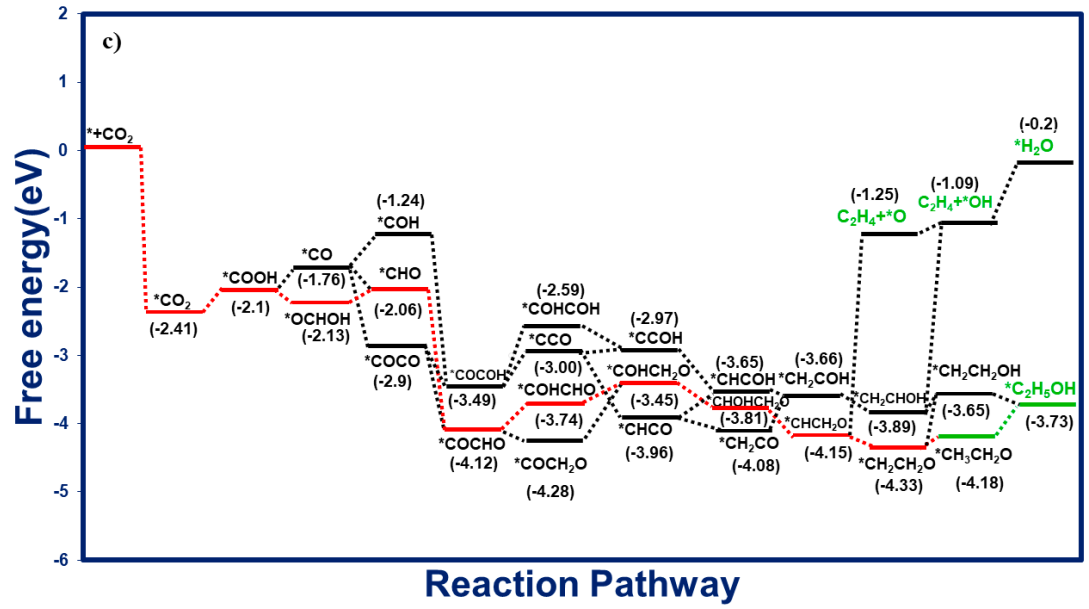


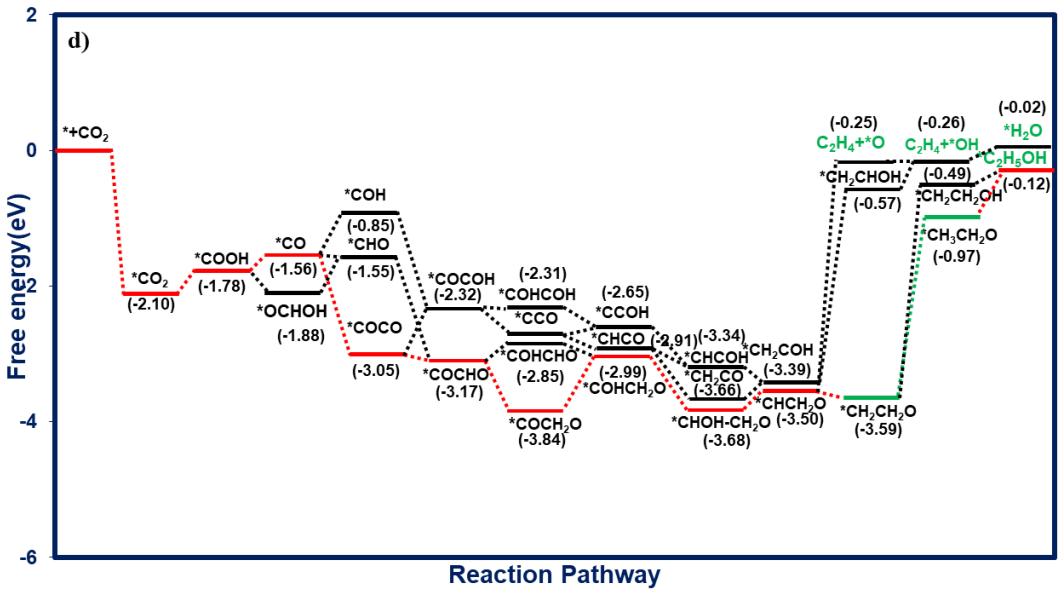
Fig. S5: *Detailed computed free energy diagram representing the various possible pathways for the reduction of CO_2 to C_1 products on a) Cr_2NbC_2 b) Cr_2TaC_2 c) Cr_2TiC_2 d) Cr_2VC_2 e) Mo_2NbC_2 f) Mo_2TaC_2 g) Mo_2TiC_2 h) Mo_2VC_2 i) Ti_2NbC_2 j) Ti_2TaC_2 k) V_2TaC_2 l) V_2TiC_2. The*

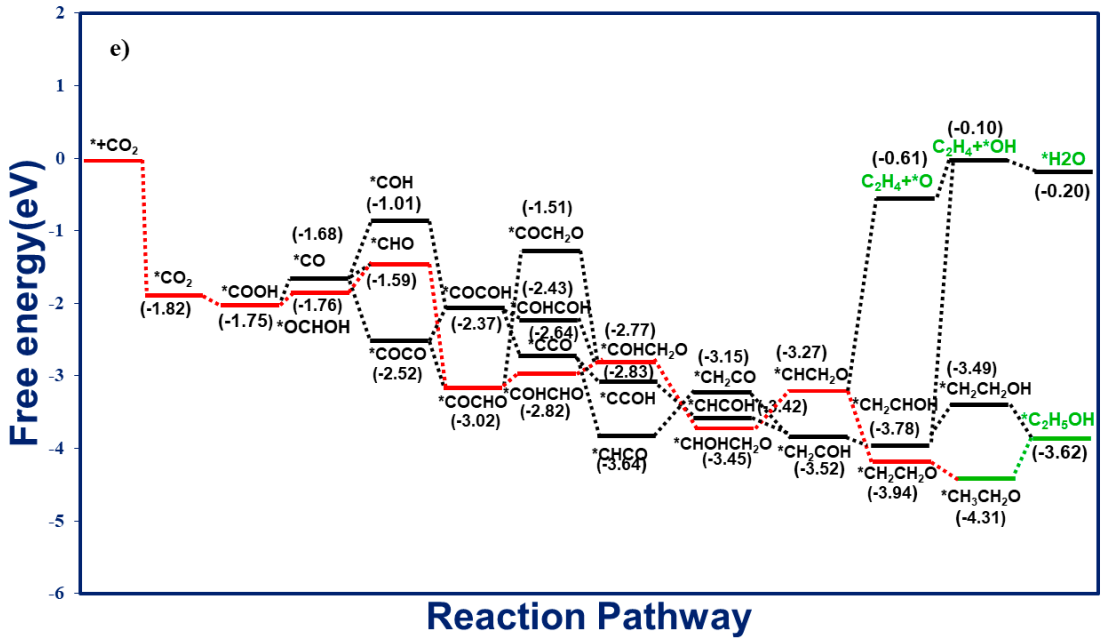
most favourable pathways are highlighted in red colour with the potential determining steps represented by green colour.

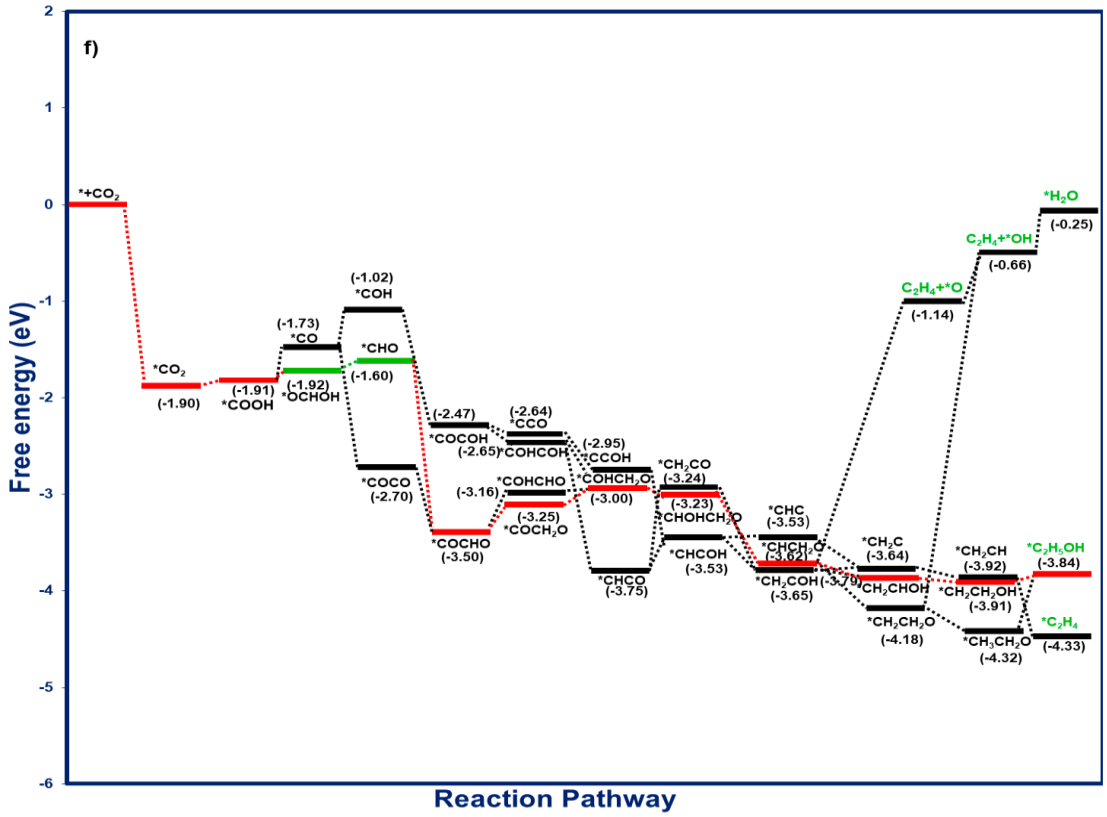

a)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2 (-2.55)
*COOH (-2.22)
*CO (-1.93)
*OHCOH (-2.36)
*COH (-1.47)
*CHO (-2.04)
*COCO (-2.83)
*COCOH (-2.63)
*COCHO (-3.66)
(-2.57) *COHCOH
(-3.21) *CCO
(-3.28) *COHCHO
*COCH2O (-3.63)
(-2.82) *CCOH
*CHCO (-3.19)
(-3.43) *COHCH2O
(-3.53) *CHCOH
*CH2CO (-4.03)
*CHOH-CH2O (-4.16)
*CH2COH (-3.77)
(-3.95) *CHCH2O
C2H4+*O (-0.92)
*CH2CHOH (-3.94)
(-4.4) *CH2CH2O
C2H4+*OH (-1.13)
*CH2CH2OH (-4.1)
*CH3CH2O (-4.65)
*H2O (-0.76)
*C2H5OH (-4.13)

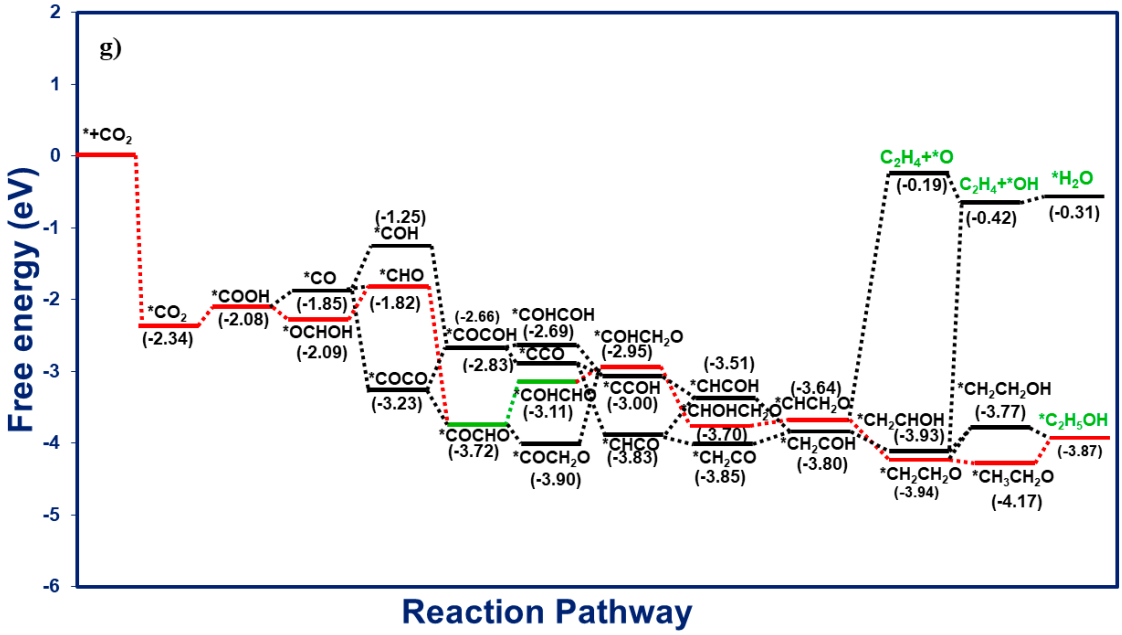

b)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2 (-1.92)
*COOH (-1.41)
*CO (-1.12)
*OHCOH (-1.49)
(-0.65) *COH
*CHO (-1.26)
*COCO (-2.08)
*COCOH (-2.25)
*COCHO (-2.74)
(-1.74) *COHCOH
(-2.20) *CCO
*COHCHO (-2.68)
*COCH2O (-3.31)
(-1.89) *CCOH
(-2.90) *CHCO
*COHCH2O (-3.22)
(-2.39) *CHCOH
*CHOH-CH2O (-3.09)
*CH2CO (-3.47)
*CH2COH (-2.48)
*CHCH2O (-3.2)
C2H4+*O (-0.17)
(-3.21) *CH2CHOH
*CH2CH2O (-3.7)
C2H4+*OH (-0.38)
*CH2CH2OH (-3.39)
*CH3CH2O (-3.92)
*H2O (0.05)
*C2H5OH (-3.48)

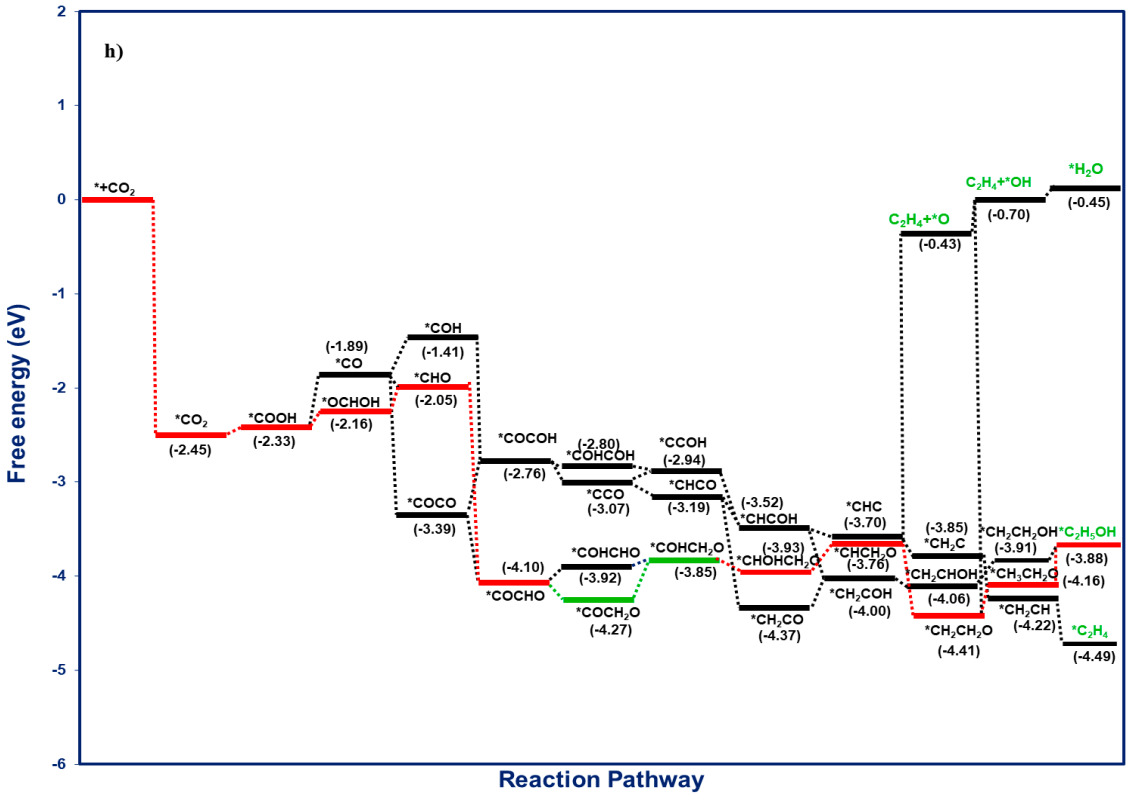

c)
Free energy(eV)
Reaction Pathway
*+CO2
*CO2 (-2.41)
*COOH (-2.1)
*CO (-1.76)
*OCHOH (-2.13)
(-1.24) *COH
*CHO (-2.06)
*COCO (-2.9)
*COCOH (-3.49)
*COCHO (-4.12)
(-2.59) *COHCOH
*CCO (-3.00)
*COHCHO (-3.74)
*COCH2O (-4.28)
(-2.97) *CCOH
*COCHO2 (-3.45)
*CHCO (-3.96)
(-3.65) *CHCOH
*CHOCH2O (-3.81)
*CH2CO (-4.08)
(-3.66) *CH2COH
*CHCH2O (-4.15)
(-1.25) C2H4+*O
*CH2CHOH (-3.89)
*CH2CH2O (-4.33)
(-1.09) C2H4+*OH
*CH2CH2OH (-3.65)
*CH3CH2O (-4.18)
(-0.2) *H2O
*C2H5OH (-3.73)

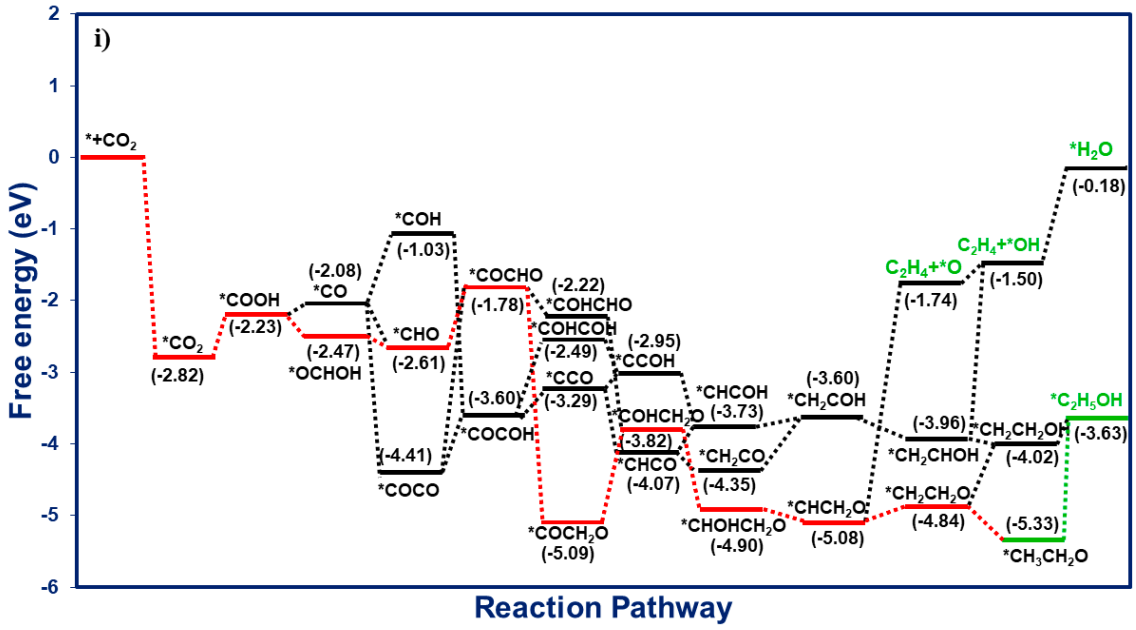

d)
Free energy(eV)
Reaction Pathway
*+CO2
*CO2
(-2.10)
*COOH
(-1.78)
*CO
(-1.56)
*OCHOH
(-1.88)
*COH
(-0.85)
*CHO
(-1.55)
*COCO
(-3.05)
*COCOH
(-2.32)
*COCHO
(-3.17)
(-2.31)
*COHCOH
*CCO
*COHCHO
(-2.85)
*COCH2O
(-3.84)
(-2.65)
*CCOH
*CHCO
(-2.91)
(-2.99)
*COHCH2O
(-3.34)
*CHCOH
*CH2CO
(-3.66)
*CHOH-CH2O
(-3.68)
*CH2COH
(-3.39)
*CHCH2O
(-3.50)
*CH2CH2O
(-3.59)
(-0.25)
C2H4+*O
*CH2CHOH
(-0.57)
(-0.26)
C2H4+*OH
(-0.49)
*CH2CH2OH
*CH3CH2O
(-0.97)
(-0.02)
*H2O
C2H5OH
(-0.12)

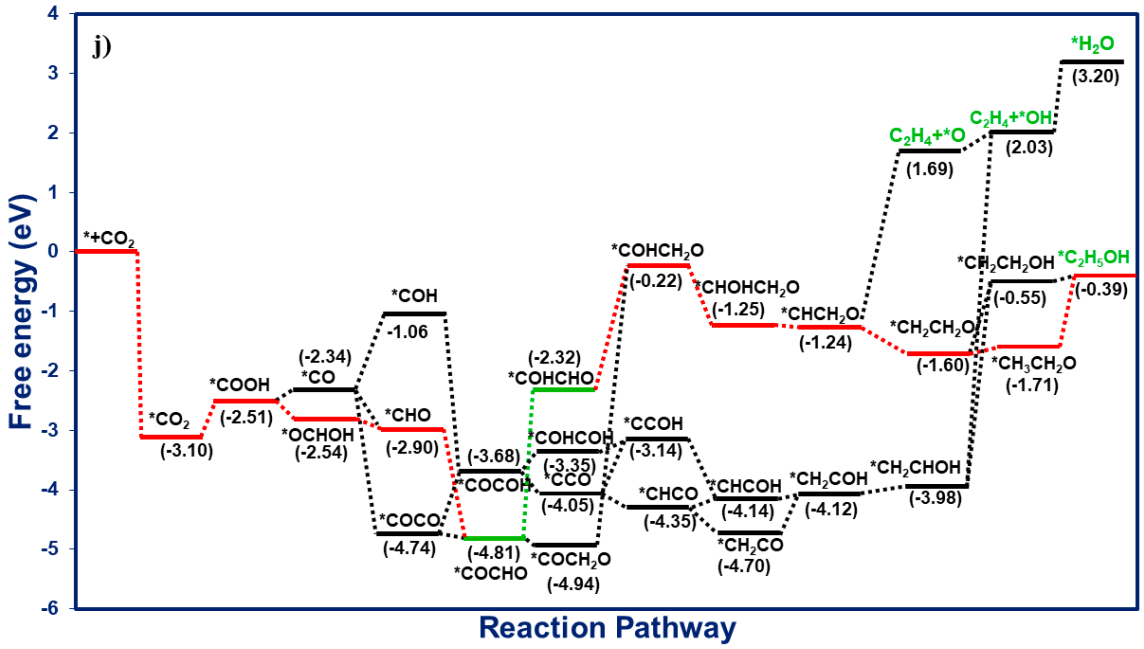

e)
Free energy(eV)
Reaction Pathway
*+CO2
*CO2
(-1.82)
*COOH
(-1.75)
*OCHOH
(-1.76)
*CO
(-1.68)
*COH
(-1.01)
*CHO
(-1.59)
*COCO
(-2.52)
*COCOH
(-2.37)
*COCHO
(-3.02)
(-1.51)
*COCH2O
(-2.43)
*COHCOH
(-2.64)
*CCO
*COHCHO
(-2.82)
(-2.77)
*COHCH2O
(-2.83)
*CCOH
*CHCO
(-3.64)
(-3.15)
*CH2CO
*CHCOH
(-3.42)
*CHOHCH2O
(-3.45)
(-3.27)
*CHCH2O
*CH2COH
(-3.52)
(-0.61)
C2H4+*O
*CH2CHOH
(-3.78)
*CH2CH2O
(-3.94)
(-0.10)
C2H4+*OH
(-3.49)
*CH2CH2OH
*CH3CH2O
(-4.31)
*H2O
(-0.20)
*C2H5OH
(-3.62)

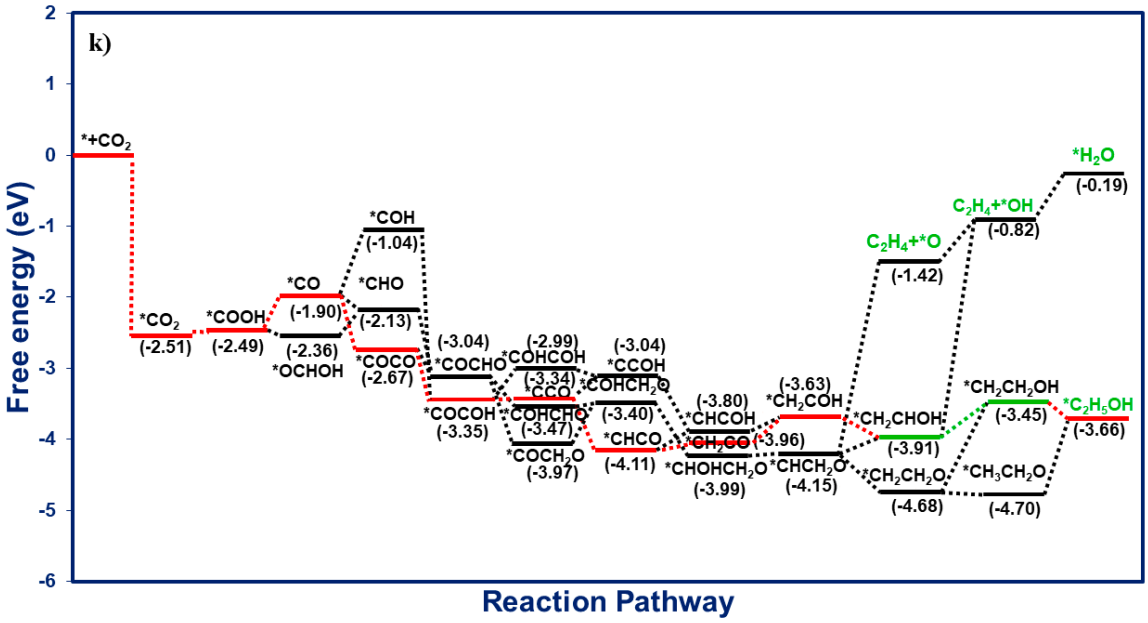

f)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2
(-1.90)
(-1.91)
*COOH
(-1.73)
*CO
(-1.92)
*OCHOH
(-1.02)
*COH
*CHO
(-1.60)
*COCO
(-2.70)
(-2.47)
*COCOH
(-2.65)
*COCHO
(-3.50)
(-2.64)
*CCO
*COHCOH
(-3.16)
*COHCHO
(-3.25)
*COCH2O
(-2.95)
*CCOH
*COHCH2O
(-3.00)
*CHCO
(-3.75)
*CH3CO
(-3.24)
(-3.23)
*CHOHCH2O
*CHCOH
(-3.53)
*CHC
(-3.53)
*CHCH2O
(-3.62)
*CH2COH
(-3.65)
(-3.70)
*CH2C
(-3.64)
*CH2CHOH
*CH2CH2O
(-4.18)
C2H4+*O
(-1.14)
C2H4+*OH
(-0.66)
*H2O
(-0.25)
*CH2CH
(-3.92)
*CH2CH2OH
(-3.91)
*CH3CH2O
(-4.32)
*C2H5OH
(-3.84)
*C2H4
(-4.33)


g)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2
(-2.34)
*COOH
(-2.08)
*OCHOH
(-2.09)
*CO
(-1.85)
(-1.25)
*COH
*CHO
(-1.82)
*COCO
(-3.23)
(-2.66)
*COCOH
(-2.83)
*COCHO
(-3.72)
*COHCOH
(-2.69)
*CCO
*COHCHO
(-3.11)
*COCH2O
(-3.90)
*COHCH2O
(-2.95)
*CCOH
(-3.00)
*CHCO
(-3.83)
(-3.51)
*CHCOH
*CHOHCH2O
(-3.70)
*CH2CO
(-3.85)
(-3.64)
*CHCH2O
*CH2COH
(-3.80)
*CH2CHOH
(-3.93)
*CH2CH2O
(-3.94)
C2H4+*O
(-0.19)
C2H4+*OH
(-0.42)
*H2O
(-0.31)
*CH2CH2OH
(-3.77)
*CH3CH2O
(-4.17)
*C2H5OH
(-3.87)


h)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2
(-2.45)
*COOH
(-2.33)
(-1.89)
*CO
*OCHOH
(-2.16)
*COH
(-1.41)
*CHO
(-2.05)
*COCO
(-3.39)
*COCOH
(-2.76)
(-2.80)
*COHCOH
*CCO
(-3.07)
*CCOH
(-2.94)
*CHCO
(-3.19)
(-4.10)
*COCHO
*COHCHO
(-3.92)
*COCH2O
(-4.27)
*COHCH2O
(-3.85)
(-3.52)
*CHCOH
(-3.93)
*CHOHCH2O
*CH2CO
(-4.37)
*CHC
(-3.70)
*CHCH2O
(-3.76)
*CH2COH
(-4.00)
C2H4+*O
(-0.43)
(-3.85)
*CH2C
*CH2CHOH
(-4.06)
*CH2CH2O
(-4.41)
C2H4+*OH
(-0.70)
*CH2CH2OH
(-3.91)
*CH3CH2O
(-4.16)
*CH2CH
(-4.22)
*H2O
(-0.45)
*C2H5OH
(-3.88)
*C2H4
(-4.49)


i)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2
(-2.82)
*COOH
(-2.23)
(-2.08)
*CO
(-2.47)
*OCHOH
*COH
(-1.03)
*CHO
(-2.61)
(-4.41)
*COCO
*COCHO
(-1.78)
(-3.60)
*COCOH
(-2.22)
*COHCHO
*COHCOH
(-2.49)
*CCO
(-3.29)
*COCH2O
(-5.09)
(-2.95)
*CCOH
*COHCH2O
(-3.82)
*CHCO
(-4.07)
*CHCOH
(-3.73)
*CH2CO
(-4.35)
*CHOHCH2O
(-4.90)
(-3.60)
*CH2COH
*CHCH2O
(-5.08)
C2H4+*O
(-1.74)
(-3.96)
*CH2CHOH
*CH2CH2O
(-4.84)
C2H4+*OH
(-1.50)
*CH2CH2OH
(-4.02)
(-5.33)
*CH3CH2O
*H2O
(-0.18)
*C2H5OH
(-3.63)


j)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2
(-3.10)
*COOH
(-2.51)
*OCHOH
(-2.54)
(-2.34)
*CO
*COH
-1.06
*CHO
(-2.90)
*COCO
(-4.74)
(-3.68)
*COCOH
(-4.81)
*COCHO
(-2.32)
*COHCHO
COHCOH
(-3.35)
*CCO
(-4.05)
*COCH2O
(-4.94)
*COHCH2O
(-0.22)
*CCOH
(-3.14)
*CHCO
(-4.35)
*CHOHCH2O
(-1.25)
*CHCOH
(-4.14)
*CH2CO
(-4.70)
*CHCH2O
(-1.24)
*CH2COH
(-4.12)
*CH2CH2O
(-1.60)
*CH2CHOH
(-3.98)
C2H4+*O
(1.69)
C2H4+*OH
(2.03)
*H2O
(3.20)
*CH2CH2OH
(-0.55)
*C2H5OH
(-0.39)
*CH3CH2O
(-1.71)


k)
Free energy (eV)
Reaction Pathway
*+CO2
*CO2
(-2.51)
*COOH
(-2.49)
*OCHOH
(-2.36)
*CO
(-1.90)
*COH
(-1.04)
*CHO
(-2.13)
*COCO
(-2.67)
(-3.04)
*COCHO
*COCOH
(-3.35)
(-2.99)
*COHCOH
(-3.34)
*CCO
*COHCHO
(-3.47)
*COCH2O
(-3.97)
(-3.04)
*CCOH
*COHCH2O
(-3.40)
*CHCO
(-4.11)
(-3.80)
*CHCOH
*CH2CO
(-3.99)
*CHOHCH2O
(-3.63)
*CH2COH
(-3.96)
*CHCH2O
(-4.15)
C2H4+*O
(-1.42)
*CH2CHOH
(-3.91)
*CH2CH2O
(-4.68)
C2H4+*OH
(-0.82)
*H2O
(-0.19)
*CH2CH2OH
(-3.45)
*C2H5OH
(-3.66)
*CH3CH2O
(-4.70)

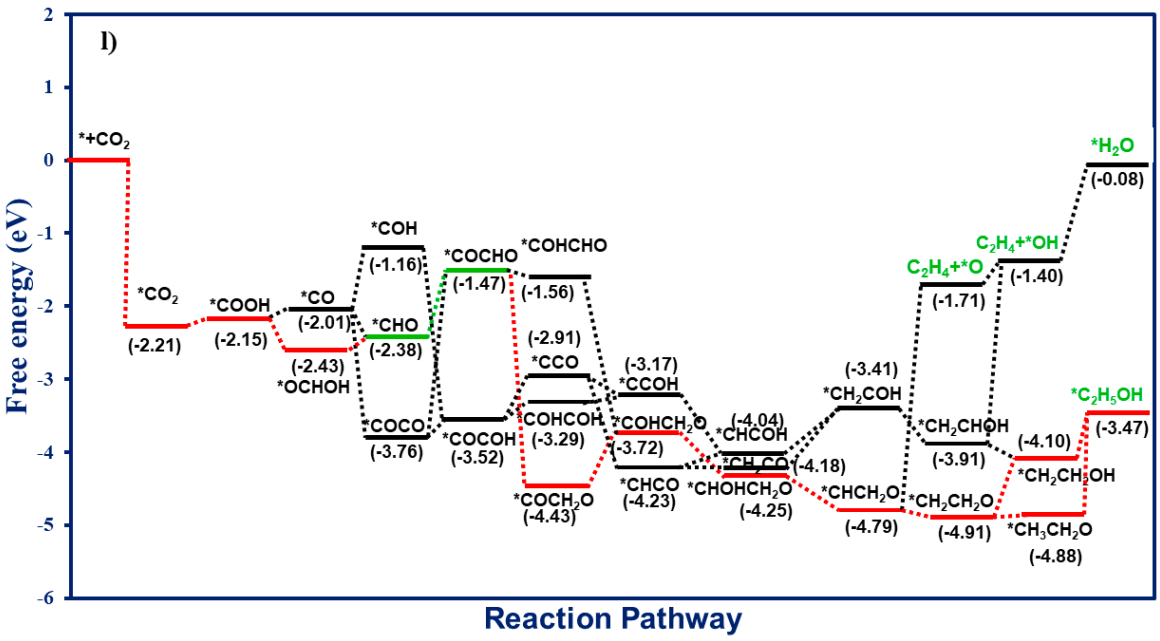


Fig. S6: *Detailed computed free energy diagram representing the various possible pathways for the reduction of CO_2 to C_2 products on a) Cr_2NbC_2 b) Cr_2TaC_2 c) Cr_2TiC_2 d) Cr_2VC_2 e) Mo_2NbC_2 f) Mo_2TaC_2 g) Mo_2TiC_2 h) Mo_2VC_2 i) Ti_2NbC_2 j) Ti_2TaC_2 k) V_2TaC_2 l) V_2TiC_2. The most favourable pathways are highlighted in red colour with the potential determining steps represented by green colour.*

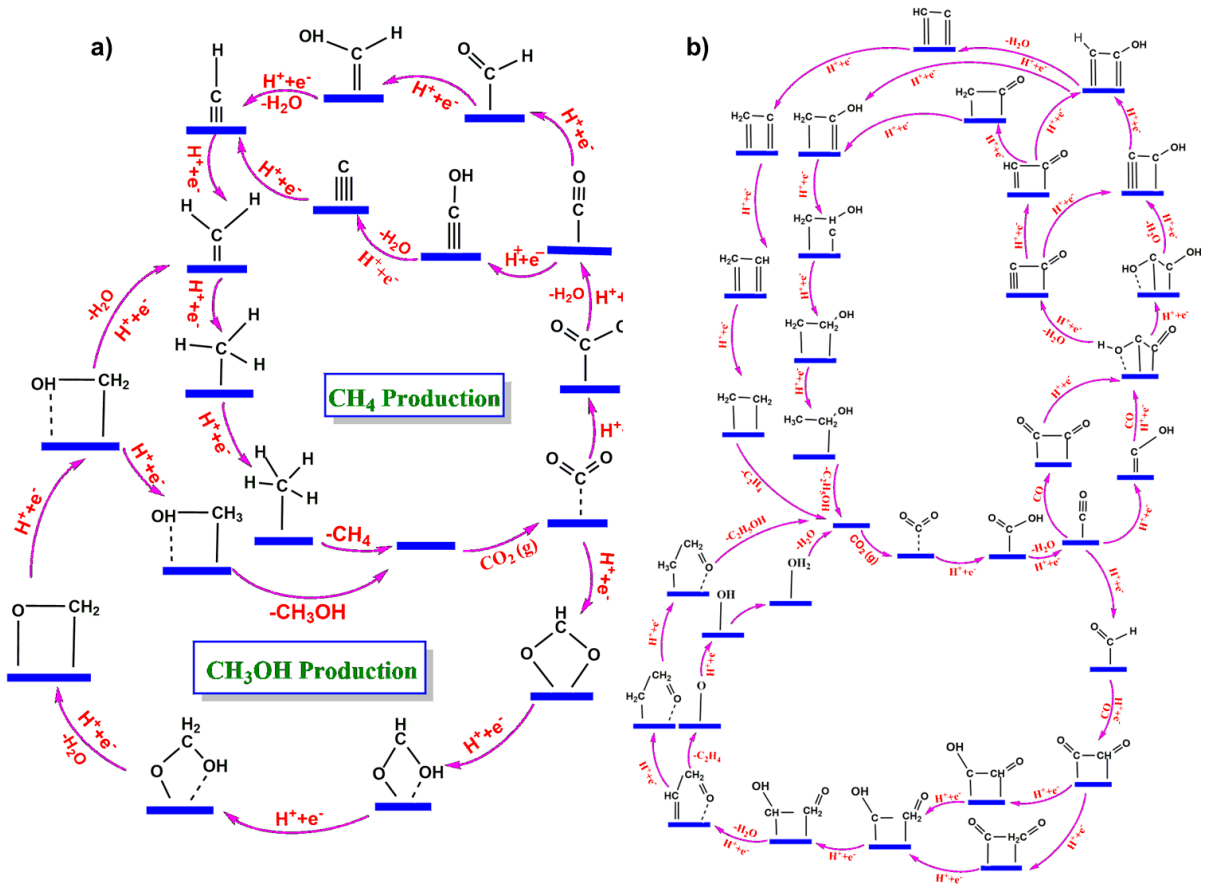


Fig. S7: *Proposed reaction mechanism for CO_2 reduction to a) C_1 products (CH_4 and CH_3OH) and b) C_2 products (C_2H_4 and C_2H_5OH) on MXenes.*

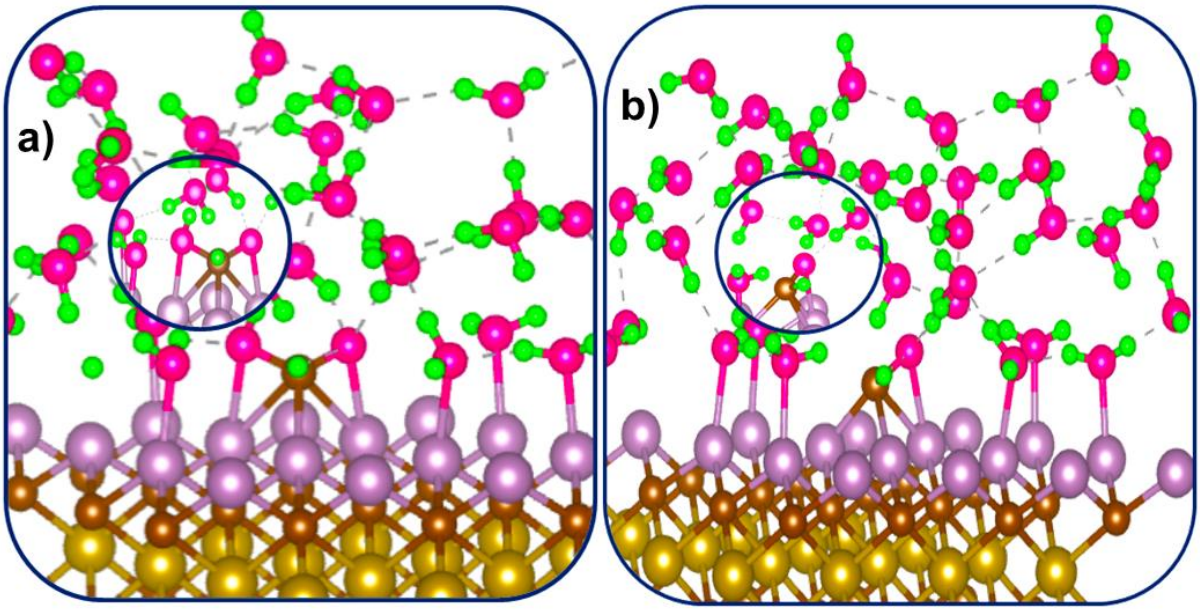


Fig S8: Electrode/Solution Interface of potential determining steps of CO_2 reduction on Mo_2TaC_2 MXene: a) Initial state and b) Final state of C_2 products.

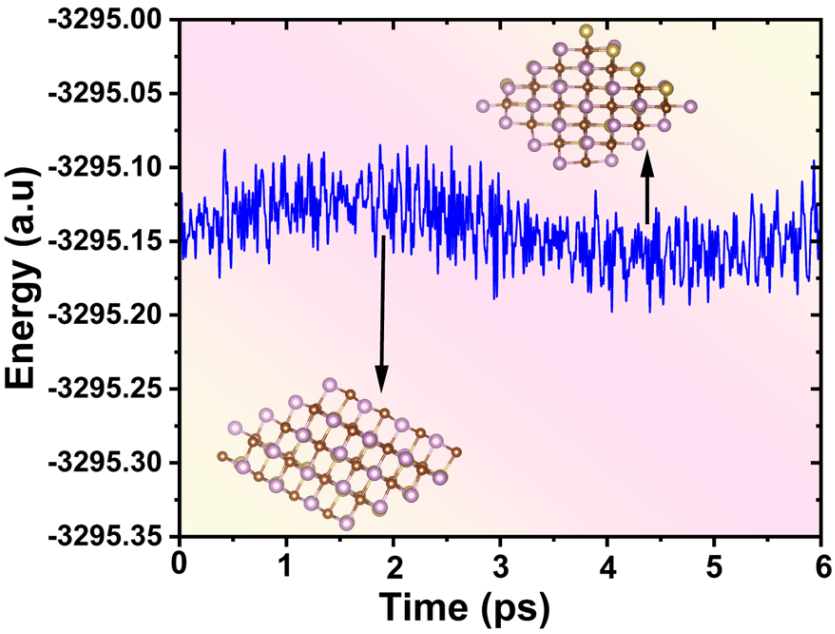


Fig. S9: *Variation of energy versus the AIMD simulation time for Mo_2TaC_2 for 6 ps at 600 K. The insets are the top views of snapshots of configurations.*